Statistical and Thermal Physics: Homework 7

Due: 14 February 2020

1 Free expansion of a gas

In a free expansion a gas that is not in thermal contact with its surroundings is allowed to expand into a vacuum region.

a) Is any work done on this gas during a free expansion? Explain your answer.

b) Noting that the gas is thermally isolated, what is that change in energy during a free expansion?

c) Suppose that the gas is an ideal gas. During a free expansion does its temperature increase or decrease? Explain your answer.

d) Suppose that the gas is a van der Waals gas. During a free expansion does its temperature increase or decrease? Explain your answer.

To make these more precise recall the identity

$$\left(\frac{\partial z}{\partial y}\right)_x = -\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z.$$

e) Use this identity and another identity (we will demonstrate this in class later)

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

to show that

$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{1}{c_V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right].$$

f) Use the previous result to confirm whether a free expansion of an ideal gas results in a temperature change. Repeat this for a van der Waals gas.

2 Extensive and intensive variables

Consider various samples of the same gas whose particle number densities $\rho = N/V$ are fixed. Recall that an extensive variable is one which is proportional to the number of particles in the system.

a) Consider various samples of an ideal gas, all at the same pressure. Rewrite the pressure and energy equations of state ρ rather than volume. Which of the following are extensive: V, T, E? Explain your answer.

b) Consider various samples of a van der Waals gas, all at the same pressure. Rewrite the pressure and energy equations of state ρ rather than volume. Which of the following are extensive: V, T, E? Explain your answer.

3 Entropy change and energy flow in constant volume processes

Consider a system that consists of two subsystems, labeled A and B, each of whose volume is fixed and whose particle number is fixed. Suppose that the two subsystems interact and undergo an infinitesimal process in which energy flows from one subsystem to another. Using only i)

$$\mathrm{d}S = \mathrm{d}S_A + \mathrm{d}S_B$$

and ii) the definition of the thermodynamic temperature,

$$T = \left(\frac{\partial S}{\partial E} \right)_{V,N}^{-1}$$

show that the second law of thermodynamics implies that energy must flow from the higher to the lower temperature subsystem as they approach equilibrium.

4 Volume change and energy flow in constant temperature processes

Consider a system that consists of two subsystems, labeled A and B, whose particle number is fixed. Suppose that the two subsystems are at the same temperature, interact and undergo an infinitesimal process in which the total volume of the pair of the systems is fixed.

a) Provide a "cartoon" diagram, indicating the systems and how they might be insulated from each other and the environment, which illustrates such a process.

b) Using only i)

$$\mathrm{d}S = \mathrm{d}S_A + \mathrm{d}S_B$$

and ii) the definition of the thermodynamic pressure,

$$P = \left(\frac{\partial S}{\partial V} \right)_{E,N}$$

show that the second law of thermodynamics implies that volume of the higher pressure system must increase as they approach equilibrium. Is it possible that energy is transferred in this process? Does this matter for the conclusion about the volume change?

2

a) No there is no surface on which to push $\Rightarrow$ $\boxed{W=0}$

b) $\Delta E = Q + W$

But $Q = 0$ $\Rightarrow$ $\Delta E = 0 + 0$ $\Rightarrow$ $\boxed{\Delta E = 0}$

c) $E = f N k T$ where $f = \frac{3}{2}, \frac{5}{2}, \ldots$

Then $\Delta E = 0$ $\Rightarrow$ $\Delta T = 0$ $\Rightarrow$ No temp change.

d) $E = f N k T - a \frac{N^2}{V}$

Then $\Delta E = 0$ $\Rightarrow$ $f N k \, \Delta T = a N^2 \Delta \left(\frac{1}{V}\right)$

If volume increases then $\Delta\left(\frac{1}{V}\right) < 0$ $\Rightarrow$ $\Delta T < 0$

$\Rightarrow$ temp drops

e) $\left(\frac{\partial T}{\partial V}\right)_E = -\left(\frac{\partial T}{\partial E}\right)_V \left(\frac{\partial E}{\partial V}\right)_T$

Now $\left(\frac{\partial E}{\partial T}\right)_V = C_V$ $\Rightarrow$ $\left(\frac{\partial T}{\partial E}\right|_V = 1 / \frac{\partial E}{\partial T}\big|_V = \frac{1}{C_V}$

$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{1}{C_V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P \right]$

f) For an ideal gas $P = \frac{N k T}{V}$ $\Rightarrow$ $\frac{\partial P}{\partial T} = \frac{N k}{V}$ $\Rightarrow$ $T\frac{\partial P}{\partial T} = \frac{N k T}{V} - P = 0$

Ideal: $\left(\frac{\partial T}{\partial V}\right)_E = 0$ $\Rightarrow$ T does not change.

For

For a v.d. Waals gas

$$\left(P + a\frac{N^2}{V^2}\right)(V-Nb) = NkT$$

$\Rightarrow \quad T = \frac{1}{Nk}\left(P + a\frac{N^2}{V^2}\right)(V-Nb)$

$\Rightarrow \quad \left(\frac{\partial T}{\partial P}\right)_V = \frac{V-Nb}{Nk}$

$\Rightarrow \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk}{V-Nb}$

$\Rightarrow \quad T\left(\frac{\partial P}{\partial T}\right)_V = \frac{NkT}{V-Nb} = P + a\frac{N^2}{V^2}$

$\Rightarrow \quad T\left(\frac{\partial P}{\partial T}\right)_V - P = +a\frac{N^2}{V^2}$

So $\quad \left(\frac{\partial T}{\partial V}\right)_E = -\frac{1}{C_V}a\frac{N^2}{V^2}$

So $\quad \frac{\partial T}{\partial V} < 0 \quad \Rightarrow \quad$ T decreases as V increases.

a) ρ is constant

Then $V = N/\rho$ $\Rightarrow$ V is proportional to $N \Rightarrow$ $\boxed{V \text{ extensive}}$

Now $PV = NkT$

$\Rightarrow$ $P = \frac{N}{V}kT$ $\Rightarrow$ $P = \boxed{\rho k} T$

constant

If P is constant as N increases then so is T $\Rightarrow$ $\boxed{T \text{ not extensive}}$

Then $E = \frac{3}{2}NkT$ $\Rightarrow$ E proportional to N $\Rightarrow$ $\boxed{E \text{ extensive}}$

constant

b) By same reasoning V is extensive

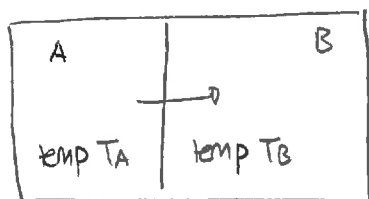Then

$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = NkT$$

$\Rightarrow$ $\underbrace{(P + a\rho^2)}_{\text{const}} \underbrace{(1 - \rho b)}_{\text{const}} = \underbrace{\rho kT}_{\text{const}}$ $\Rightarrow$ T constant regardless of N

$\Rightarrow$ $\boxed{T \text{ not extensive}}$

Finally

$$E = \frac{3}{2}NkT - a\frac{N^2}{V}$$

$\Rightarrow E = N\underbrace{\left(\frac{3}{2}kT - a\rho\right)}_{\text{const}}$ $\Rightarrow$ E proportional to N $\Rightarrow$ $\boxed{E \text{ extensive}}$

$$E = E_A + E_B$$

$$S = S_A + S_B$$

We need $\qquad dS \geq 0$

But $\qquad dS = dS_A + dS_B$

$$= \left(\frac{\partial S_A}{\partial E_A}\right)_{V_A, N_A} dE_A + \left(\frac{\partial S_A}{\partial V_A}\right)_{E_A, N_A} \cancel{dV_A}^{0} + \left(\frac{\partial S_A}{\partial N_A}\right)_{E_A, V_A} \cancel{dN_A}^{0}$$

$$+ \left(\frac{\partial S_B}{\partial E_B}\right) dE_B + \quad \cdots \cancel{}^{0} \quad + \quad \cdots \cancel{}^{0}$$
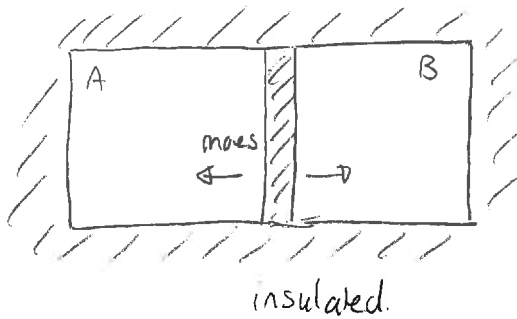
Then $\quad dE_A = - dE_B.$ gives $\qquad dS = \left[\left(\frac{\partial S_A}{\partial E_A}\right) - \left(\frac{\partial S_B}{\partial E_B}\right)\right] dE_A$

$$= \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dE_A$$

$$\Rightarrow \quad \left[\frac{1}{T_A} - \frac{1}{T_B}\right] dE_A \geq 0$$

Suppose $\quad T_A > T_B \quad$ then $\quad \frac{1}{T_A} - \frac{1}{T_B} \leq 0 \Rightarrow dE_A \leq 0$

which implies energy leaves A if A has higher temp

insulated.

b) $dS = dS_A + dS_B$

$$= \frac{\partial S_A}{\partial E_A} dE_A + \frac{\partial S_B}{\partial E_B} dE_B + \frac{\partial S_A}{\partial V_A} dV_A + \frac{\partial S_B}{\partial V_B} dV_B.$$

Constant total energy $\Rightarrow$ $E = E_A + E_B$ const $\Rightarrow 0 = dE_A + dE_B$

$$\Rightarrow dE_B - dE_A$$

Similar for volume. So

$$dS = \frac{1}{T_A} dE_A - \frac{1}{T_B} dE_A + \frac{P_A}{T_A} dV_A - \frac{P_B}{T_B} dV_A$$

$$= \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dE_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right) dV_A$$

If at one moment temps are same then

$$dS = \frac{1}{T} (P_A - P_B) dV_A \geqslant 0$$

If $P_A > P_B$ then $dV_A > 0$ $\Big\}$ higher pressure volume
      $P_A < P_B$ then $dV_A < 0$ $\Big\}$ increases.

Yes energy could be transfered. At the same temp it does not matter
            $\hookrightarrow$ one gas does work on the other